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The Reactions of Alkynlcyclophazenes with Metal Carbonyls

by

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<p>ABSTRACT The reactions of $N_3P_3F_3C\equiv CR$ ($R=Ph, Me_3Si, n-C_4H_9$) with $Co_2(CO)_8$ lead to $N_3P_3F_3C\equiv CRCo_2(CO)_6$. The corresponding reaction with $2,2-N_3P_3F_4(C\equiv CPh)_2$ produces the novel, structurally characterized, tetracobalt species $2,2-N_3P_3F_4(C\equiv CPh)_2Co_4(CO)_6$. In the case of the previously reported $N_3P_3F_3C\equiv CPh$ complex, we now report that reaction with excess ligand leads to the cyclotrimerized material $1,2,4-(N_3P_3F_3)_3Ph_3C_6(I)$. Detailed dynamic ^{19}F NMR spectroscopy studies of this material shows detectable barriers to rotation about the phosphorus-carbon bond of the central arene. The reaction of a more reactive catalyst, $\eta^5-C_5H_5Co(CO)_2$, with $N_3P_3F_3C\equiv CPh$ gives rise to a variety of cyclooligomerized products. A cyclodimerized material, $(N_3P_3F_3)_2Ph_2C_2(II)$ is isolated as the cobalt stabilized entity $II\cdot CoCp$. The carbonyl insertion product of the cyclodimerized complex has been isolated as well as I and its cobalt complex $I\cdot CoCp$ (which is believed to contain an η^1 arene). The reaction of $Fe(CO)_5$ with $N_3P_3F_3C\equiv CPh$ gives the iron stabilized cyclodimer, $II\cdot Fe(CO)_2$. The corresponding reaction with $Fe_2(CO)_9$ gives a plethora of products including the cyclodimerized material noted above and its carbonyl insertion product. Other characterized products include $I\cdot Fe(CO)_3$ (also believed to be an η^1 material), an iron containing metallocycle and unique derivative in which the alkyne bridges iron and cyclopentadienone fragments.</p>					
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THE REACTIONS OF ALKYNLCYCLOPHOSPHAZENES WITH METAL CARBONYLS

CHRISTOPHER W. ALLEN*, PAULINE MALIK, ADAM BRIDGES, JAMES DESORCIE AND BRIAN PELLON, Department of Chemistry University of Vermont, Burlington, VT 05405 USA.

Abstract The reaction of $N_3P_3F_3C\equiv CR$ ($R=Ph, Me_3Si, n-C_4H_9$) with $Co_2(CO)_8$ leads to $N_3P_3F_3C\equiv CR\cdot Co_2(CO)_6$. The corresponding reaction with $2,2-N_3P_3F_4(C\equiv CPh)_2$ produces the novel, structurally characterized, tetracobalt species $2,2-N_3P_3F_4(C\equiv CPh\cdot Co_2(CO)_6)_2$. In the case of the previously reported $N_3P_3F_3C\equiv CPh$ complex, we now report that reaction with excess phosphazene leads to the cyclotrimerized material $1,2,4-(N_3P_3F_3)_3Ph_3C_6(I)$. Detailed dynamic ^{19}F NMR spectroscopy studies of this material shows detectable barriers to rotation about the phosphorus-carbon bond of the central arene. The reaction of a more reactive catalyst, $\eta^5-C_5H_5Co(CO)_2$, with $N_3P_3F_3C\equiv CPh$ gives rise to a variety of cyclooligomerized products. A cyclodimerized material, $(N_3P_3F_3)_2Ph_2C_2(II)$ is isolated as the cobalt stabilized entity $II\cdot CoCp$. The carbonyl insertion product of the cyclodimerized complex has been isolated as well as I and its cobalt complex $I\cdot CoCp$ (which is believed to contain an η^4 arene). The reaction of $Fe(CO)_5$ with $N_3P_3F_3C\equiv CPh$ gives the iron stabilized cyclodimer, $II\cdot Fe(CO)_3$. The corresponding reaction with $Fe_2(CO)_9$ gives a plethora of products including the cyclodimerized material noted above and its carbonyl insertion product. Other characterized products include $I\cdot Fe(CO)_3$ (also believed to be an η^4 material), an iron containing metallocycle and unique derivative in which the alkyne bridges iron and cyclopentadienone fragments.

INTRODUCTION

In recent years it has been shown that the range of cyclo- and polyphosphazene derivatives can be dramatically expanded by synthetic transformations of organofunctional units attached to the phosphorus atoms.^{1,2} In previous, and ongoing, investigations we have explored the reactions of alkenes attached to cyclophosphazenes particularly with respect to polymer synthesis.³ A logical extension of this interest would be to investigate the reactions of alkynes attached to cyclophosphazenes. Previous work in this area is restricted to the preparation of $N_3P_3F_3C\equiv CPh\cdot Co_2(CO)_6$ by Chivers⁴ and a study by Allcock et.al. of the cyclotrimerization of propargylchlorocyclotriphosphazenes and cocyclotrimerization of propynylchlorocyclotriphosphazenes and acetylenes all through the alkyne bridged dicobalt hexacarbonyl derivatives.⁵ Given these initial studies and the tremendous range of chemistry which has been reported from metal carbonyl mediated reactions of alkynes,⁶ we have begun a systematic study of the reactions of alkynylphosphazenes with low valent transition metal complexes. The aims of these studies include construction of

RESULTS AND DISCUSSION

alkynyl and phosphazene moieties. *known*

I

IIa M=Co; L_n=η⁵C₅H₅
b M=Fe; L_n=(CO)₃

INSPECTED

Codes

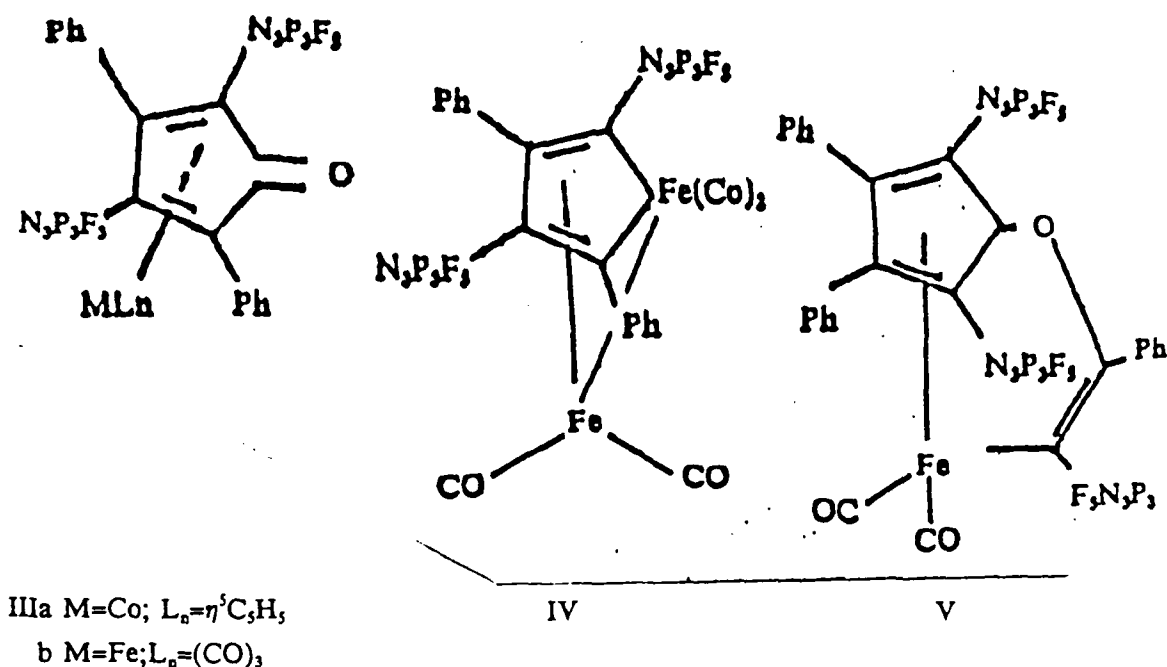
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The reaction of the known⁴ $N_3P_3F_3C\equiv CPh\cdot Co_2(CO)_8$ complex with excess $N_3P_3F_3C\equiv CPh$ produces a cyclotrimerized material, $(N_3P_3F_3)_3Ph_3C_6(I)$. The ^{19}F NMR spectrum in the fast exchange limit shows that the major component is the 1,2,4-regio isomer about the central arene (as shown for I). A small amount of the symmetric (1,3,5) isomer was also observed. The ratio of the symmetrical to unsymmetrical regio isomers can be significantly increased if $Ni(PPh_3)_4$ is used as the cyclooligomerization catalyst. Full line shape analysis of the dynamic ^{19}F NMR spectra shows that restricted rotation occurs about the phosphorus-carbon bond in I and that all three phosphazenes rotate at different rates.

In order to expand the range of cobalt mediated chemistry, the reactions of a more active catalyst, $CpCo(CO)_2$, with $N_3P_3F_3C\equiv CPh$ were explored under a wide variety of conditions. The major products derived from these reactions include the cobalt stabilized cyclodimerized material IIa, for which a crystal structure has been determined, its carbonyl insertion product, IIIa, the cyclotrimer (I) and its cobalt complex I $\cdot CoCp$. Both electron counting considerations and electrochemical evidence suggest that the central arene to cobalt coordination in I $\cdot CoCp$ is of the η^4 type. In contrast to the reactions of $Co_2(CO)_8$, $CpCo(CO)_2$ induces cyclooligomerization for other alkynylphosphosphazenes, e.g. $N_3P_3F_3C\equiv C-n-C_4H_9$, in addition to $N_3P_3F_3C\equiv CPh$.



The chemistry of iron carbonyl-alkynylphosphazene interactions is even more complex than that observed for cobalt mediated reactions. The reaction of the coordinately saturated $Fe(CO)_5$ with $N_3P_3F_3C\equiv CPh$ is sluggish but does yield the iron

stabilized cyclodimer IIb. The crystal structure of IIb has been determined. The corresponding reactions with $\text{Fe}_2(\text{CO})_9$ give a plethora of products including the stabilized cyclodimer, IIb, and its carbonyl insertion product IIIb. A iron complex of I, $\text{I} \cdot \text{Fe}(\text{CO})_5$, which is also believed to exhibit η^4 iron-central arene coordination, has been isolated. In addition to these materials and numerous trace level products, the iron metallocycle IV and a high relative yield of the unique species V have been isolated. The structure of V has been determined by x-ray crystallography and may be considered to arise from an unusual reaction of a coordinated cyclobutadienone with an alkyne. It is of interest to note that the proposed cyclobutadiene $\bullet\text{Fe}(\text{CO})_5$ precursor to V results from a head to head addition of alkynes as opposed to the head to tail addition which produces IIb.

In conclusion, it is clear that a wide range of new exocyclic groups can be constructed on cyclophosphazenes using transition metal-alkylphosphazene reactions and that in certain cases novel reactions or products are observed.

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